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(54) Title: MEDIUM AND SYSTEM FOR HYDROGEN STORAGE

(57) Abstract: The invention provides a medium and method for hydrogen storage, the medium comprising a carbon scaffold loaded with MgH₂ particles, preferably nanoparticles. Preferably the medium comprises a mesoporous carbon scaffold doped with a non-metal such as nitrogen or phosphorus.



MEDIUM AND SYSTEM FOR HYDROGEN STORAGE

FIELD OF INVENTION

[0001] The present invention relates to the field of chemical storage of hydrogen.

[0002] In one form, the invention relates to a novel medium and method of hydrogen storage.

BACKGROUND ART

[0003] It is to be appreciated that any discussion of documents, devices, acts or knowledge in this specification is included to explain the context of the present invention. Further, the discussion throughout this specification comes about due to the realisation of the inventor and/or the identification of certain related art problems by the inventor. Moreover, any discussion of material such as documents, devices, acts or knowledge in this specification is included to explain the context of the invention in terms of the inventor's knowledge and experience and, accordingly, any such discussion should not be taken as an admission that any of the material forms part of the prior art base or the common general knowledge in the relevant art in Australia, or elsewhere, on or before the priority date of the disclosure and claims herein.

[0004] Hydrogen (H_2) has been regarded as an ideal energy carrier with nearly zero pollution and high energy density (142 MJ/kg). One of the key challenges towards the large scale use of H_2 fuel is the storage. Many different methods of hydrogen storage have been described in the prior art including physical storage methods using high pressure, cryogenics and chemical storage using compounds that reversibly release H_2 when heated.

[0005] A large number of chemical storage systems involving hydrolysis reactions, hydrogenation/dehydrogenation reactions, ammonia borane and other boron hydrides, ammonia, and alane and so forth are under investigation. Most metal hydrides bind strongly with hydrogen and metal hydrides including MgH_2 , $NaAlH_4$, $LiAlH_4$, LiH , $LaNi_5H_6$, $TiFeH_2$ and palladium hydride have also been investigated as storage media. Some are easy-to-fuel liquids at ambient temperature and pressure, others are solids which could

be turned into pellets. These materials have good energy density by volume, although their energy density by weight is often worse than the leading hydrocarbon fuels. Among these solid hydrides, magnesium is particularly promising due to its low cost and high storage capacity.

[0006] Because metal hydrides bind strongly with hydrogen relatively high temperatures (around 120 – 200°C) must be applied to release their hydrogen content. This energy cost can be reduced by using alloys which consists of a strong hydride former and a weak one such as in LiNH_2 , LiBH_4 and NaBH_4 but if the interaction is too weak, the pressure needed for rehydriding is high, thereby eliminating any energy savings. The target for onboard hydrogen fuel systems is roughly <100°C for release and 20–60 kJ/mol H_2 for recharge.

[0007] Magnesium hydride (MgH_2) has attracted extensive attention due to its excellent hydrogen storage capacity (7.6 wt% H_2) and low cost but desorption of the hydrogen is problematic. In particular, the practical application is restricted by the sluggish kinetics and high desorption temperature ($T_{\text{des}} > 283^\circ\text{C}$) for starting release of hydrogen.

[0008] To address this issue, various technologies have been developed, such as doping, ball milling, and nano confinement. For instance, T_{des} can be reduced remarkably if ultra-small MgH_2 nanoparticles are employed. It has been reported that nanoparticles of 0.9 nm corresponding to $T_{\text{des}} \approx 200^\circ\text{C}$ (Kim et al, Nanotechnology 20, 204001 (2009); Wagemans et al, J.Am.Chem.Soc. 127, 16675 (2005); Wu et al, J.Am.Chem.Soc. 131(39), 13918 (2009)) but the disadvantage is that such small particles would be sintered or aggregated during the following hydrogen absorption and desorption cycles.

[0009] In an attempt to overcome this problem, nano-confinement strategy has been proposed – MgH_2 nano particles have been confined in porous scaffolds, such as metal organic framework (MOF), carbon materials CMK-3, carbon aerogel, and mesoporous silicon. Jia et al. (Phys.Chem. 15(16) 5814 (2013) report that loading MgH_2 into ordered mesoporous carbon (CMK-3) allows hydrogen release to start at a temperature of only 50°C.

[0010] Accordingly there is an ongoing need to identify hydrogen storage systems that have high storage capacity and are convenient and practical for sorption and desorption of hydrogen.

SUMMARY OF INVENTION

[0011] An object of the present invention is to provide a chemical storage system for hydrogen that allows desorption of hydrogen at lower energy cost.

[0012] A further object of the present invention is to alleviate at least one disadvantage associated with the hydrogen storage systems of the related art.

[0013] It is an object of the embodiments described herein to overcome or alleviate at least one of the above noted drawbacks of related art systems or to at least provide a useful alternative to related art systems.

[0014] In a first aspect of embodiments described herein there is provided a medium for hydrogen storage, the medium comprising a carbon scaffold loaded with MgH_2 particles, preferably nanoparticles.

[0015] Preferably the medium for hydrogen storage comprises a mesoporous carbon scaffold having nano-sized pores of 1-10 nm, preferably 3 to 5 nm, prior to doping or loading. Typically the carbon scaffold has a Brunauer-Emmett-Teller (BET) surface area of 1000-1600 m^2/g , more typically 1300-1500 m^2/g prior to doping or loading. Typically, after doping the BET surface area of the doped and scaffold is reduced remarkably, such as $< 600 \text{ m}^2/\text{g}$.

[0016] Preferably the carbon scaffold includes a non-metal dopant such as nitrogen or phosphorus, typically at the time it is loaded. Typically the dopant would be present in the range of 0.6-2.2 wt.%, more typically 1.0-2.0 wt%. Nitrogen and phosphorus can reduce the reaction energy for releasing one hydrogen molecule from 0.75 eV (bulk MgH_2) to less than 0.55 eV, phosphorous reaching 0.20 eV.

[0017] Without wishing to be bound by theory, it is believed that the incorporation of non-metal atoms into a carbon network may cause local distortion and change the original electron distribution and consequently activate a part of the carbon atoms that remarkably enhances the hydrogen release properties of nanoconfined MgH_2 at comparatively low temperatures. After non-metal doping, such as with nitrogen or phosphorous, magnesium loading levels of 25-30wt% can be achieved.

[0018] In another aspect of embodiments described herein there is provided a medium for hydrogen storage, the medium comprising a scaffold of mesoporous carbon (CMK-3) loaded with MgH_2 nanoparticles and doped with a non-metal, wherein hydrogen desorption starts at a temperature as low as 50°C , with $\sim 1.5\text{wt}\%$ released below 200°C . Preferably the medium has a hydrogen desorption capacity of at least $0.8\text{ wt}\%$ below 150°C , and/or at least $1.5\text{ wt}\%$ below 200°C and/or at least $2.8\text{ wt}\%$ below 250°C .

[0019] In yet a further aspect of embodiments described herein there is provided a hydrogen storage system comprising a medium according to the present invention.

[0020] In another aspect of embodiments described herein there is provided a method of storing hydrogen comprising the steps of:

- adsorbing hydrogen into the medium of the present invention, and
- desorbing at least some of said hydrogen from the medium of the present invention at a temperature of less than 250°C , preferably less than 200°C .

[0021] In another aspects of embodiment described herein there is provide a method of manufacturing a medium for hydrogen storage comprising the steps of:

- forming a mesoporous carbon scaffold having nano-sized pores and a Brunauer-Emmett-Teller surface area of 1000 to $1600\text{ m}^2/\text{g}$, and,
- doping the scaffold with a non-metal dopant, chosen from nitrogen or phosphorous present at a level of 0.6 to $2.2\text{ wt}\%$, wherein doping reduces

the Brunauer-Emmett-Teller surface area of the scaffold to less than 600 m²/g.

[0022] The method of manufacture typically includes the further step of loading the carbon scaffold with magnesium hydride nanoparticles to a magnesium loading level of 25 to 30 wt%. The resultant loaded and doped medium preferably has a hydrogen desorption capacity of at least 1.5 wt% at a desorption temperature (T_{des}) of 200°C.

[0023] Other aspects and preferred forms are disclosed in the specification and/or defined in the appended claims, forming a part of the description of the invention.

[0024] In essence, embodiments of the present invention stem from the realization that better hydrogen storage performance may be achieved by optimising interfacial bonding between magnesium and a confinement environment. In particular, the invention stems from the realization that the combination of non-metal (particularly phosphorus) doping and nano-confinement can be used to overcome the impractically high desorption temperature required to take advantage of the hydrogen storage capacity of magnesium hydride (MgH₂). Without wishing to be bound by theory, besides the effect of nano-confinement, the charge transfer from MgH₂ to the carbon scaffold may play a role in the significant improvement of MgH₂ dehydrogenation.

[0025] Advantages provided by the present invention comprise the following:

- uses lower hydrogen desorption temperatures compared with the prior art,
- lower energy cost due to use of lower hydrogen desorption temperatures,
- easier processing due to use of lower hydrogen desorption temperatures.

[0026] Uses for the medium of the present invention extends to a wide range of industrial process that require an economically viable carrier material for hydrogen storage and release on demand. In a preferred application, the medium of the present invention is used in conjunction with regenerative fuel cells, such as hydrogen-bromine regenerative fuel cells.

[0027] Furthermore the hydrogen fuel may be a counterpart to use of oxidizers other than oxygen, such as bromine, to provide an energy storage alternative for grid level needs.

[0028] Further scope of applicability of embodiments of the present invention will become apparent from the detailed description given hereinafter. However, it should be understood that the detailed description and specific examples, while indicating preferred embodiments of the invention, are given by way of illustration only, since various changes and modifications within the spirit and scope of the disclosure herein will become apparent to those skilled in the art from this detailed description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0029] Further disclosure, objects, advantages and aspects of preferred and other embodiments of the present application may be better understood by those skilled in the relevant art by reference to the following description of embodiments taken in conjunction with the accompanying drawings, which are given by way of illustration only, and thus are not limitative of the disclosure herein, and in which:

FIG. 1 illustrates aspects of the computational screening of dopants. FIG. 1a depicts a model of CMK-3 filled with an MgH_2 cluster including C (1), Mg (3) and H (5) and dopants (X) (7) shown; FIG. 1b illustrates the calculated average value of desorption energy for $\text{MgH}_2@\text{X}_{12}\text{-CMK3}$ Er with $\text{X}=\text{P}$, N, B, and S (9), with the data for bulk case (11), pure $\text{Mg}_{38}\text{H}_{76}$ cluster (13) and undoped ($\text{X} = \text{C}$) structures listed as reference.

FIG. 2 depicts an XPS survey with peaks corresponding to O1s (15), C1s (17) and P2p (19) (FIG. 2a) and a high resolution C1s spectrum (FIG. 2b), O1s spectrum (FIG. 2c), and P2p spectrum (FIG. 2d) of an as-prepared P-doped CMK-3 sample.

FIG. 3 depicts an HRTEM image of P/CMK-3 (FIG. 3a) and $\text{MgH}_2@\text{P/CMK-3}$ (FIG. 3b).

FIG. 4 depicts a TPD-MS spectra (FIG. 4a) of $\text{MgH}_2@\text{CMK-3}$ (19), $\text{MgH}_2@\text{P}/\text{CMK-3}$ (21) and CMK-3 (23) measured with a heating rate of $5^\circ\text{C}/\text{min}$ under Ar flowing gas; and, hydrogen desorption kinetics curves of $\text{MgH}_2@\text{CMK-3}$ (25) and $\text{MgH}_2@\text{P}/\text{CMK-3}$ (27) measured at the temperature (29) from room temperature to 143°C , 191°C , 241°C , 291°C , 341°C , 391°C and kept different time (heating rate $10^\circ\text{C}/\text{min}$). Hydrogen content was normalized to theoretical capacity (FIG. 4b).

DETAILED DESCRIPTION

[0030] The following describes a computational investigation and experimental validation of phosphorus (P)-modified CMK-3 as a scaffold for MgH_2 (hereafter referred to as $\text{MgH}_2@\text{P}/\text{CMK-3}$).

[0031] In summary, the hydrogen desorption energy of $\text{Mg}_{76}\text{H}_{152}$ clusters with or without non-metal dopants were calculated by density functional theory method. Phosphorus (P), identified as the best dopant, can reduce the reaction energy for releasing one hydrogen molecule from 0.75 eV (bulk MgH_2) to 0.20 eV. Based on the calculation, P-doped ordered mesoporous carbon (CMK-3) was synthesized by one-step method and employed as the scaffold for loading MgH_2 nanoparticles, forming $\text{MgH}_2@\text{P}/\text{CMK-3}$. Elemental analysis showed the phosphorus dopants had been incorporated into the CMK-3 scaffold and magnesium and phosphorus elements were well-distributed in carbon scaffold hosts. Tests of hydrogen desorption confirmed that P-doping can remarkably enhance the hydrogen release properties of nanoconfined MgH_2 at low temperature, specifically approximately 1.5wt.% H_2 being released from $\text{MgH}_2@\text{P}/\text{CMK-3}$ below 200°C . This demonstrated that the combined approach of non-metal doping and nano-confinement is promising for enhancing the hydrogen desorption properties of MgH_2 , which provides a strategy to address the challenge of hydrogen desorption from MgH_2 at mild operational conditions.

[0032] **Computational Investigation:** A computational investigation of four non-metal dopants ($\text{X}=\text{B}$, N , S , and P) was carried out, with a focus on whether these heteroatoms can destabilize MgH_2 confined by CMK-3 scaffold. The calculations were performed under the scheme of standard density functional theory with Perdew-Burke-

Ernzerhof functional for the exchange-correlation term, (Perdew et al, Phys.Rev.Lett. 77(18) 3865 (1996)) as embedded in the Vienna ab-initio Simulation Package (VASP) (Kresse & Joubert, Phys.Rev.B 59(3) 1758 (1999))

[0033] During the calculation, the projector augmented wave method with a cutoff energy of 400 eV was been employed to achieve high computational efficiency. CMK-3 was modelled by a cubic supercell with a pore as shown in FIG. 1(a), in which dopants (blue spheres) are introduced to replace carbon, followed with full relaxation with MgH_2 or Mg clusters. The desorption energy (DE) is calculated by $\text{DE} = (E(\text{MgH}_2@\text{C}) - E(\text{Mg}@\text{C}) - nE(\text{H}_2))/n$, where $E(\text{MgH}_2@\text{C})$ and $E(\text{Mg}@\text{C})$ are the energy of MgH_2 and Mg clusters confined in CMK-3, and $E(\text{H}_2)$ and n are the energy of single H_2 molecule and the number of H_2 molecules released from the system. Given the desorption of surface hydrogen and bulk hydrogen is quite different, the calculations only consider the averaged DE with hydrogen fully released.

[0034] FIG. 1(b) shows the calculated DE, with the data of bulk MgH_2 and unconfined cluster $\text{Mg}_{76}\text{H}_{152}$ as the reference. For bulk MgH_2 , DE is as high as 0.75 eV per H_2 , as determined by the strong Mg-H bonding. For $\text{Mg}_{76}\text{H}_{152}$ clusters, DE is reduced to 0.62 eV with respect to the bulk case – the improvement being attributed to the size effect. When it is confined in CMK-3 (corresponding to $X = \text{C}$), DE can be further reduced to 0.55 eV, due to the confinement effect. Among the four dopants, only N and P reduced DE further, and in particular the P-dopants achieved a value as low as $\text{DE} = 0.2$ eV per H_2 .

[0035] To validate the computational predication, P-modified CMK-3 was used as a scaffold to confine MgH_2 clusters. Experimentally, a one-step nano-casting method was employed to synthesize high surface area P/CMK-3 using SBA-15 as a hard template.

[0036] Briefly, the carbon replica was prepared by infiltrating the mesopores of 1.0 g SBA-15 with 1.25 g of sucrose dissolved in 5.0 ml of water containing 0.14 g H_2SO_4 and 0.5 g H_3PO_4 at the room temperature. The obtained composite was dried at 100°C for 12 h and at 160°C for another 12 h, and subsequently was completely carbonized at 850°C for 5 h in a nitrogen atmosphere. After carbonization the SBA-15 silica template was removed by etching in a 7.5 % HF solution to obtain silica-free P/CMK-3 scaffold.

[0037] Subsequently $\text{MgH}_2@\text{P}/\text{CMK-3}$ was synthesized following a study reported by Zhang et al (Nanotechnology 20, 204027 (2009)). The $\text{P}/\text{CMK-3}$ scaffold with 20 ml of MgBu_2 solution was first sealed into an autoclave and hydrogenated at 170°C under a H_2 pressure of 50 ~ 55 bar, and the MgH_2 incorporated $\text{P}/\text{CMK-3}$ was obtained after drying MgH_2 precipitate. Additionally, MgH_2 incorporated CMK-3 (non-P doping) was also prepared for comparing, named as $\text{MgH}_2@\text{CMK-3}$.

[0038] Microstructural characteristics were evaluated using X-ray diffractometer (XRD, Rigaku D/MAX-2200) and transmission electron microscopy (JEOL JEM-2010F). N_2 sorption isotherms were measured using nitrogen adsorption apparatus (ASAP 2020) X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, UK) was used in the surface analysis of the samples. Hydrogen desorption properties were examined using a temperature programmed desorption with mass spectrometry (TPD-MS) measurement and a purpose-made Sieverts' PCT apparatus.

[0039] The surface area and pore size of the synthesized $\text{MgH}_2@\text{CMK-3}$ and $\text{MgH}_2@\text{P}/\text{CMK-3}$ samples were determined by N_2 adsorption-desorption isotherms. The N_2 physi-sorption analysis of CMK-3 and $\text{P}/\text{CMK-3}$ shows a representative IV type isotherm, indicating a high uniformity of mesopores. P-doping makes the BET surface area decline slightly, from $1423 \text{ m}^2/\text{g}$ to $1044 \text{ m}^2/\text{g}$, but $\text{P}/\text{CMK-3}$ still exhibits relative high surface area. However, when MgH_2 was loaded in the carbon scaffold, BET surface area decreases remarkably, only $600 \text{ m}^2/\text{g}$ and $359 \text{ m}^2/\text{g}$ for $\text{MgH}_2/\text{CMK-3}$ and $\text{MgH}_2@\text{P}/\text{CMK-3}$, respectively. Additionally, after MgH_2 loading for P doped/non-doped carbon scaffolds, only one third of pore volume remains in both cases. Decreased BET surface area and pore volume suggest that the mesoporous structure was degraded as a result of MgH_2 highly confined in the carbon mesopores.

[0040] The successful doping of phosphorus into the ordered mesoporous carbon of CMK-3 was verified by the XPS measurements as shown in FIG. 2.

[0041] The XPS survey spectrum of P-doped CMK-3 given in FIG. 2a shows a predominant peak at 284.4 eV corresponding to C1s, a peak at 532.4 eV to O1s, and a peak at 133.5 eV to P2p. Quantitative XPS analysis shows that phosphorus is present with ~5.48 %, which is much higher than the value obtained from chemical analysis

result (1.82 at.%). We know that the XPS analysis gives the value only on the very surface but chemical analysis shows that in the whole sample.

[0042] The high-resolution C1s XPS spectrum (Fig. 2b) can be deconvolved into two different components located at about 284.4 and 285.6 eV, which can be attributed to C–C and C–P bonding, respectively. The presence of the C–P peak confirms that P atoms have been successfully intercalated into the carbon lattice.

[0043] The O1s peak (FIG. 2c) can be deconvolved into three component peaks. The peak at 531.7 eV may result from physically absorbed oxygen molecules.^{24,25} The major peak at 532.8 eV can be assigned to the P–O bonding, indicating that the O1s peak arises mainly from the chemical adsorption of oxygen.²⁵ The peak at 534.1 eV can be attributed to the C–O bonding.²⁵

[0044] The high-resolution P2p spectrum (FIG. 2d) reveals that phosphorus was doped into graphene in two main types of chemical bonding: P–C and P–O bonding at about 133.2 eV and 134.4 eV, respectively. The results strongly suggest that the phosphorus atoms are incorporated into the CMK-3 framework.

[0045] HR-TEM measurement was also carried on the synthesized P/CMK-3 and MgH₂@P/CMK-3. As shown in FIG. 3a, a pore size of around 4.0 nm in diameter can be observed in the ordered mesoporous P/CMK-3.

[0046] After MgH₂ loading, the distinct ordered pore structure displayed in P/CMK-3 was partly destroyed (FIG. 3b), which is consistent with the findings in N₂ sorption isotherms, e.g., BET surface area and pore volume are remarkably decreased. To further confirm the dispersion of confined MgH₂ nano particles, the element mapping of Mg and P was analyzed by EDX and the results are given in the FIG. 3c and 3d, indicating that MgH₂ nanoparticles are well-distributed in P/CMK-3 scaffold hosts.

[0047] Calculation results shows that DE decreases markedly by doping heteroatoms, and among them P is the best choice.

[0048] To further verify the effect of P-doping on the desorption properties of MgH_2 confined in the scaffold of CMK-3, the hydrogen desorption behaviour of $\text{MgH}_2@\text{CMK-3}$ and $\text{MgH}_2@\text{P/CMK-3}$ was examined using TPD-MS and volumetric method.

[0049] The TPD-MS profiles and hydrogen desorption kinetics curves are shown in FIG. 4a and FIG. 4b, respectively. The as-prepared CMK-3 was also hydrogenated under H_2 with a pressure of 55 bar at 170°C and totally the same condition as the hydrogenation procedure of MgBu_2 .

[0050] As shown in FIG. 4a, the sample of $\text{MgH}_2@\text{CMK-3}$ starts to release hydrogen at $\sim 50^\circ\text{C}$, but the hydrogen release rate is very slow at the temperature lower than 280°C . At the temperature above 280°C , the hydrogen desorption rate speeds up obviously, and desorption peak is centred at $\sim 380^\circ\text{C}$.

[0051] In comparison with $\text{MgH}_2@\text{CMK-3}$, the hydrogen release rate of the sample of $\text{MgH}_2@\text{P/CMK-3}$ is much faster at the low temperature zone ($30^\circ\text{C} \sim 280^\circ\text{C}$), which indicates that the P-doping could enhance the hydrogen desorption from MgH_2 , particularly at relative low temperature. In addition, as the reference, the hydrogen signal of hydrogenated CMK-3 was also examined by TPD-MS, in which case no hydrogen released until at the temperature of 400°C (Hydrogen signal above 400°C indicates that $-\text{CH}_2$ or $-\text{CH}_3$ functional groups may be formed after hydrogenation of CMK-3, which is different from the as-prepared CMK-3 reported by Jia et al. *Phys Chem* 15(16) 5814 (2013).) The result further proved that the released hydrogen at the low temperature comes from the decomposition of MgH_2 .

[0052] The TPD-MS results have proved that P-doping could enhance hydrogen release of the MgH_2 particles confined in the CMK-3 scaffold at low temperature. In order to gain further insight into the hydrogen desorption behaviour of MgH_2 by coupling P-doping and nano-confinement, volumetric method was applied for the hydrogen desorption kinetics measurement.

[0053] FIG. 4b presents hydrogen desorption kinetics curves of the samples of $\text{MgH}_2@\text{CMK-3}$ and $\text{MgH}_2@\text{P/CMK-3}$ at various temperatures. Here, the total hydrogen release capacity of two samples was normalized to theoretical hydrogen content of pure

MgH₂ (7.6 wt.%). Notably, the sample of MgH₂@P/CMK-3 released about 0.8 wt.% H₂ below 150 °C, 1.5 wt.% H₂ below 200 °C and 2.8 wt.% H₂ below 250°C. The corresponding sample of MgH₂@CMK-3 released only about 0.1, 0.3 and 0.9 wt.% H₂ at the same conditions. It is noteworthy that, the sample of MgH₂@P/CMK-3 exhibits much better desorption behaviour than MgH₂@CMK-3 at low temperature region (below 250°C).

[0054] Although the value is normalized from pure MgH₂, the observed hydrogen release capacity of MgH₂ evaluated by a volumetric method at the temperature below 150°C is very low. However, when the temperature is higher than 250°C, MgH₂@CMK-3 shows faster hydrogen desorption rate than the sample of MgH₂@P/CMK-3, which is in good agreement with TPD-MS result. The opposite behaviour in hydrogen release at the high temperature zone should be caused by the distinguishing porous structure.

[0055] Without wishing to be bound by theory, we know that the BET surface area of MgH₂@P/CMK-3 is almost half in comparison with that of MgH₂@CMK-3. Thus, it is speculated that the hydrogen desorption of MgH₂ might be mainly affected by two factors: one is the heteroatom doping on the carbon scaffold; the other one is the surface area of the carbon scaffold. On the one hand, P-doping would enhance the hydrogen desorption properties of nanoconfined MgH₂. However, in this study, P-doped content is only 1.82 wt.%, which means that the destabilization of Mg-H bond by P atoms may not be sufficient. On the other hand, the higher BET surface of porous carbon, the more MgH₂ particles embedded in the scaffold, which implies that MgH₂@CMK-3 sample with higher BET surface should have better desorption performance due to nano-confinement effect. It seems that, comparing with BET surface, phosphorus doping may have stronger influence at low temperature zone.

[0056] While this invention has been described in connection with specific embodiments thereof, it will be understood that it is capable of further modification(s). This application is intended to cover any variations uses or adaptations of the invention following in general, the principles of the invention and including such departures from the present disclosure as come within known or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth.

[0057] As the present invention may be embodied in several forms without departing from the spirit of the essential characteristics of the invention, it should be understood that the above described embodiments are not to limit the present invention unless otherwise specified, but rather should be construed broadly within the spirit and scope of the invention as defined in the appended claims. The described embodiments are to be considered in all respects as illustrative only and not restrictive.

[0058] Various modifications and equivalent arrangements are intended to be included within the spirit and scope of the invention and appended claims. Therefore, the specific embodiments are to be understood to be illustrative of the many ways in which the principles of the present invention may be practiced. In the following claims, means-plus-function clauses are intended to cover structures as performing the defined function and not only structural equivalents, but also equivalent structures.

[0059] “Comprises/comprising” and “includes/including” when used in this specification is taken to specify the presence of stated features, integers, steps or components but does not preclude the presence or addition of one or more other features, integers, steps, components or groups thereof. Thus, unless the context clearly requires otherwise, throughout the description and the claims, the words ‘comprise’, ‘comprising’, ‘includes’, ‘including’ and the like are to be construed in an inclusive sense as opposed to an exclusive or exhaustive sense; that is to say, in the sense of “including, but not limited to”.

CLAIMS

1. A medium for hydrogen storage, the medium comprising a carbon scaffold loaded with MgH_2 particles, preferably nanoparticles.
2. A medium according to claim 1 wherein the carbon scaffold is a mesoporous carbon scaffold having a typical pore size of 1 to 10 nm, preferably 3 to 5 nm prior to loading.
3. A medium according to claim 1 wherein the carbon scaffold has a Brunauer-Emmett-Teller (BET) surface area of 1000 to 1600 m^2/g , preferably 1300-1500 m^2/g prior to loading.
4. A medium according to claim 1 or claim 2 wherein the scaffold includes a non-metal dopant chosen from nitrogen or phosphorus.
5. A medium according to claim 4 wherein the dopant is present at a level of 0.6 to 2.2 wt%, preferably 1.0 to 2.0 wt%.
6. A medium for hydrogen storage, the medium comprising a scaffold of mesoporous carbon loaded with MgH_2 nanoparticles and doped with a non-metal, wherein the medium has a hydrogen desorption capacity of at least 1.5 wt% at a desorption temperature (T_{des}) of 200°C.
7. A medium according to claim 6 having a hydrogen desorption capacity of at least 0.8 wt% below 150°C
8. A medium according to claim 6 having a hydrogen desorption capacity of at least 1.5 wt% below 200°C
9. A medium according to claim 6 having a hydrogen desorption capacity of and/or at least 2.8 wt% below 250°C.

10. A hydrogen storage system comprising a medium according to any one of the previous claims.
11. A regenerative fuel cell when used in conjunction with the medium according to any one of claims 1 to 9.
12. A method of storing hydrogen comprising the steps of;
 - adsorbing hydrogen into the medium of the present invention, and
 - desorbing at least some of said hydrogen from the medium of the present invention at a temperature of less than 250°C, preferably less than 200°C.
13. A method of manufacturing a medium for hydrogen storage comprising the steps of
 - forming a mesoporous carbon scaffold having nano-sized pores and a Brunauer-Emmett-Teller surface area of 1000 to 1600 m²/g, and
 - doping the carbon scaffold with a non-metal chosen from nitrogen or phosphorous at a level of 0.6 to 2.2 wt% such that the Brunauer-Emmett-Teller surface area of the scaffold is reduced to less than 600 m²/g.
14. A method of manufacture according to claim 12 which includes the further step of:
 - loading the carbon scaffold with magnesium hydride nanoparticles to a magnesium loading level of 25 to 30 wt% wherein the resultant loaded and doped medium has a hydrogen desorption capacity of at least 1.5 wt% at a desorption temperature (T_{des}) of 200°C.
15. A method of manufacturing the medium of claim 1 using the method of claim 13.

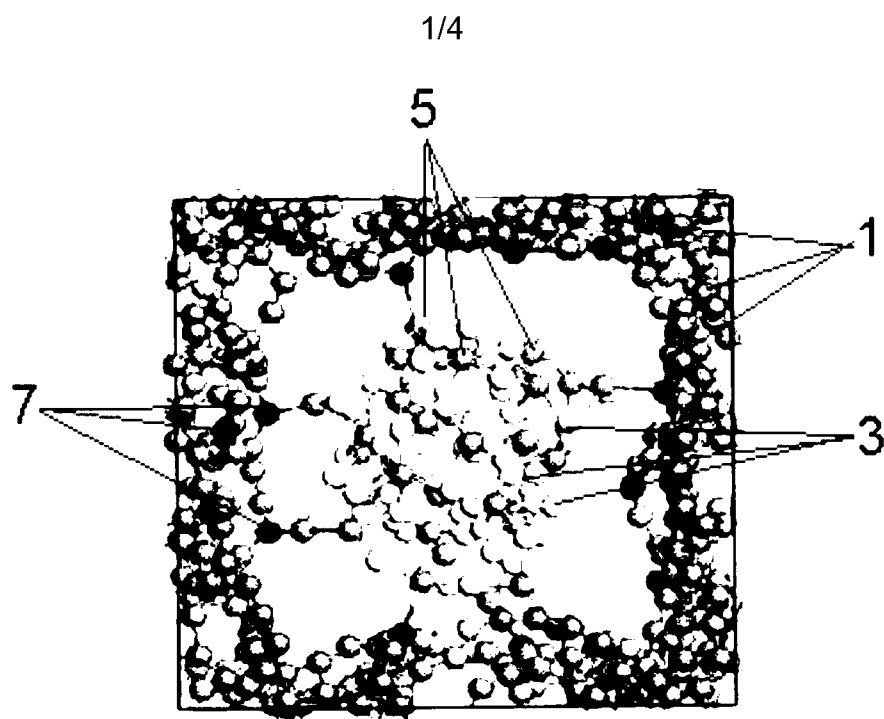


FIG. 1a

FIG. 1a

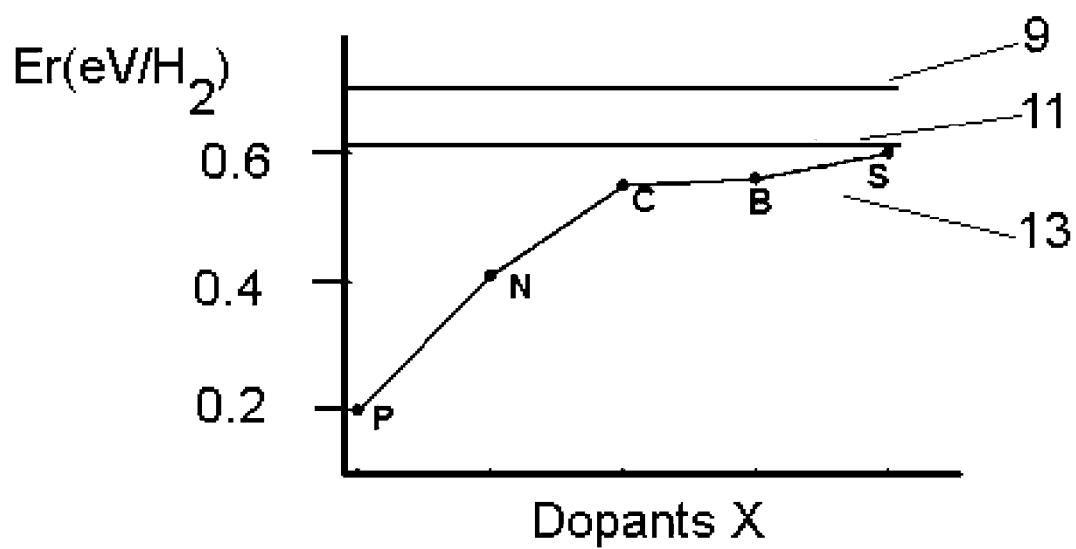


FIG. 1b

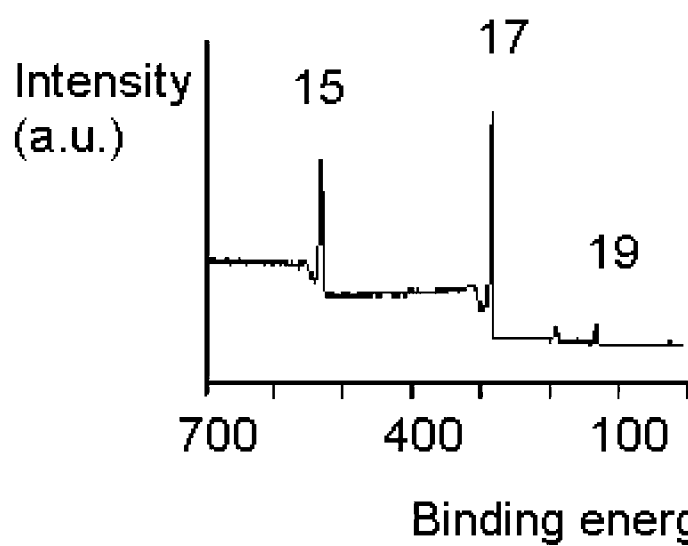


FIG. 2a

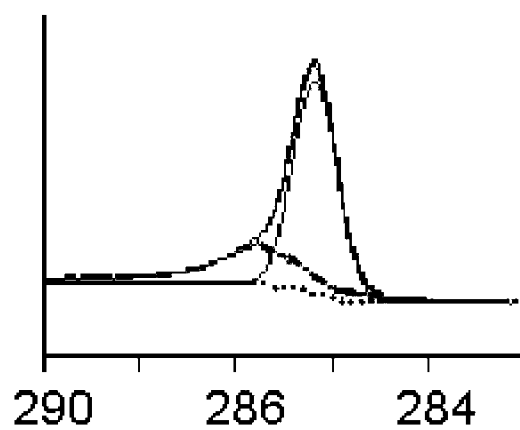


FIG. 2b

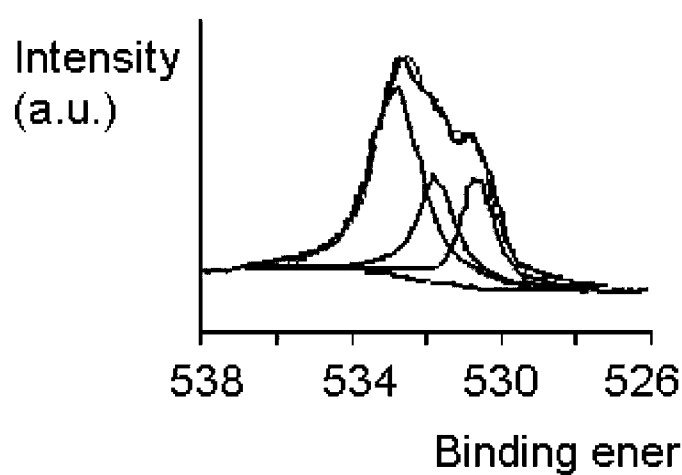


FIG. 2c

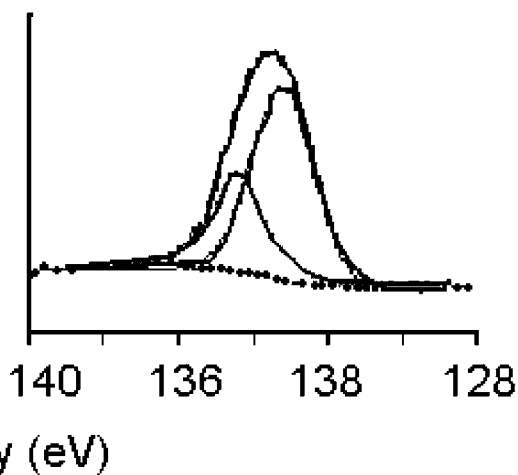


FIG. 2d



FIG. 3a

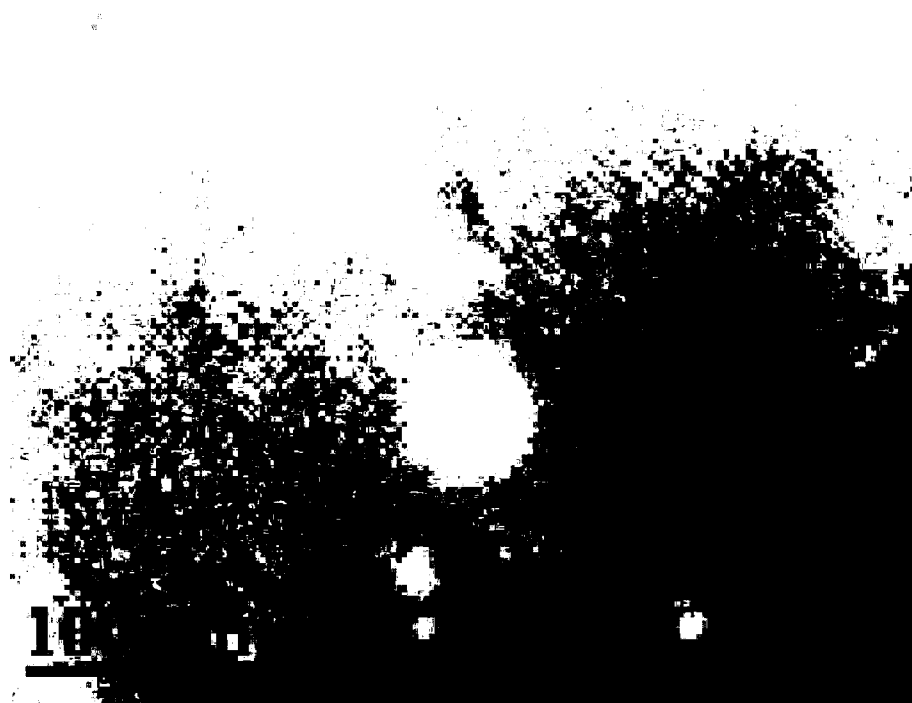


FIG. 3b

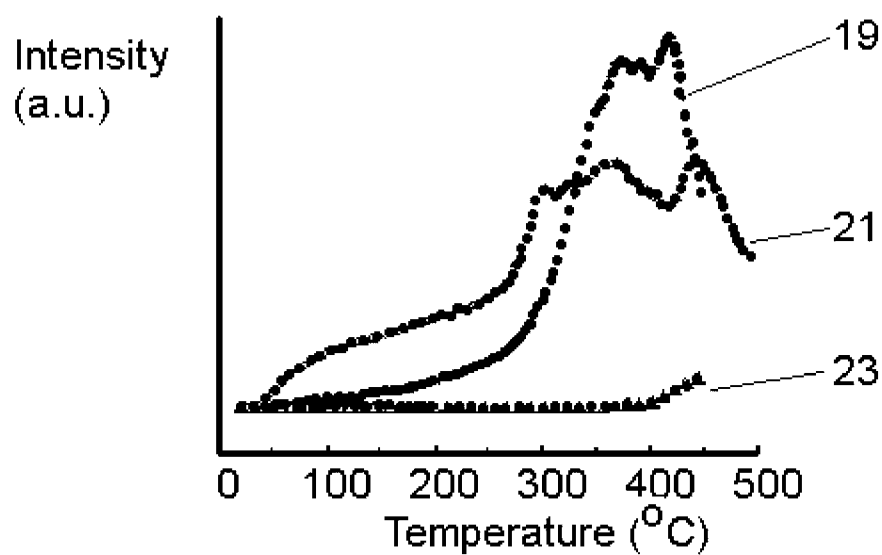


FIG. 4a

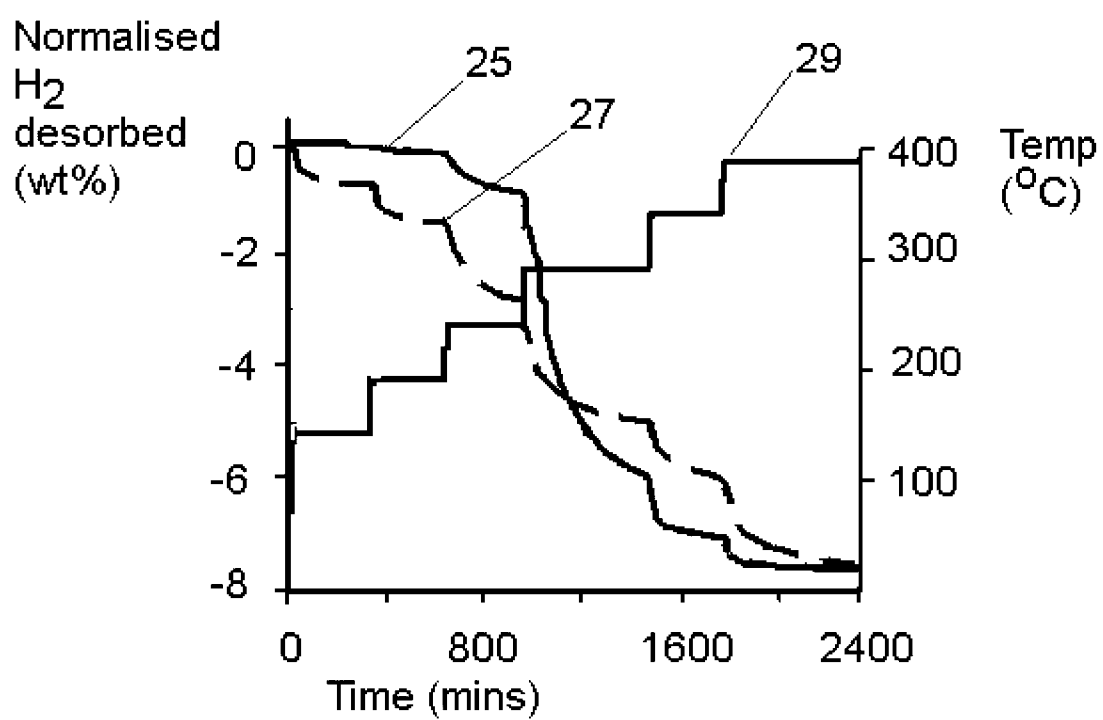


FIG. 4b

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/AU2016/000381

A. CLASSIFICATION OF SUBJECT MATTER

B01J 20/20 (2006.01) B01J 20/04 (2006.01) B01J 20/32 (2006.01) B01J 20/28 (2006.01) H01M 8/18 (2006.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPIAP, TXTE, CAPlus, COMPENDEX, INSPEC, GOOGLE, GOOGLE SCHOLAR, ESPACENET with IPC/CPC: C01B3/0021, Y02E60/325, B01J20/20/low, C01B3/0042, Y02E60/327, B01J20/04, C01B3/0078, B01J20/28026, B01J20/2805, B01J20/3204/CN, B01J20/3295, C01B3/0084, B01J20/28064, B01J20/2808, B01J20/28083, B01J20/28045/CN, H01M8/18 and/or Keywords: Hydrogen storage, magnesium hydride, CMK-3, mesoporous carbon, dibutylmagnesium and similar terms and/or truncations.

GOOGLE, CAPlus, COMPENDEX, INSPEC and IP Australia internal databases with Applicant: Monash University and Inventor: Sun, Chenghua

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 21 December 2016	Date of mailing of the international search report 21 December 2016
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au	Authorised officer Luke Sweetman AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262256163

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
the subject matter listed in Rule 39 on which, under Article 17(2)(a)(i), an international search is not required to be carried out, including
2. ☒ Claims Nos.: **12**
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
See Supplemental Box
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/AU2016/000381
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HE D. et al., 'Enhanced hydrogen desorption properties of magnesium hydride by coupling non-metal doping and nano-confinement', Applied Physics Letters, 18 December 2015, Vol. 107, Pages 243907-1 - 243907-5 Abstract, page 243907-1 right column paragraph 2, page 243907-2 left column paragraph 2 and right column lines 2-7, page 243907-4 left column paragraph 2 and Figure 1-4	1-11, 13-20
X	CN 104961099 A (SHANGHAI UNIVERSITY) 07 October 2015 Abstract, [0005]-[0006], [0008], [0012], [0015]-[0016] and Figures 3-4	1-11, 13-20
X	JIA Y. et al., 'Destabilization of Mg-H bonding through nano-interfacial confinement by unsaturated carbon for hydrogen desorption of MgH ₂ ', Physical Chemistry Chemical Physics, 2013, Vol. 15, Pages 5814-5820 Experimental section and Microstructure characterizations	1-11, 13-20
X	ZHANG S. et al., 'The synthesis and hydrogen storage properties of a MgH ₂ incorporated carbon aerogel scaffold', Nanotechnology, 2009, Vol. 20, 204027, Pages 1-6 Abstract and experimental	1-11, 13-20
X	CN 105645356 A (SHANGHAI UNIVERSITY) 08 June 2016 Abstract and detailed description	1-11, 13-20

Supplemental Box**Continuation of Box II**

Claim 12 does not comply with Rule 6.2(a) because it makes reference to a method of storing hydrogen comprising the step of absorbing hydrogen into the medium 'of the present invention'. The present invention is considered to be the invention as described by the entire specification including that of the description and/or drawings and thus does not comply with Rule 6.2(a). Consequently, search and examination of the subject matter of claim 12 has been reserved.

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/AU2016/000381	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
CN 104961099 A	07 October 2015	CN 104961099 A	07 Oct 2015
CN 105645356 A	08 June 2016	CN 105645356 A	08 Jun 2016
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			